

中国唐松草属植物的化学系统学初探

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CHEMOSYSTEMATIC STUDIES ON *THALICTRUM* L. IN CHINA

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Abstract According to chemical constituents, plant morphology and geographic distribution of *Thalictrum* in China, the relationships among sections in the genus are discussed in the present paper. The results show:

1. China is one of the major distribution centers of *Thalictrum* plants, with half of species endemic. Compared with species in other regions of the world, Chinese ones are relatively primitive.

2. From the chemosystematic point of view, the system of the genus adopted in Fl. Reip. Pop. Sin. is reasonable.

3. The main constituents of *Thalictrum* plants are benzyloquinoline alkaloids. A correlation exists between the chemical patterns and plant evolution. The different sections are of different structure types. Aporphine-benzyloquinoline and bisbenzyloquinoline are major constituents in Sect. *Leptostigma*. Sect. *Tripterium* contains mainly aporphines, but non-alkaloid compounds are principal constituents in several species. In Sects. *Thalictrum* and *Schlagintweitella* and Subgen. *Leconyrium*, types and content of alkaloids increase obviously and thus there are medicinal species. So these sections should be interested in developing some active constituents of antitumor, hypotension and antibacterium.

4. The genus occupies a special position in Ranunculaceae, as a transition to link the follicle plants and achene plants. Meanwhile, because the genus is rich in benzyloquinoline alkaloids, the opinion that the Ranunculaceae, Berberidaceae, Menispermaceae and Papaveraceae form a natural group is even more strongly supported.

Key words *Thalictrum*; Chemosystematics; benzyloquinoline alkaloids

摘要 本文根据唐松草植物所含化学成分并结合其外部形态及地理分布对属内各群的亲缘关系进行了探讨。结果表明: (1)从化学系统学角度看, 中国植物志中所安排的属内各组植物间的关系是适宜的。(2)植物中所含生物碱的种类及含量与植物的进化有一定关系。在较原始的组中, 成分的类型和含量相对较少; 而在较进化的组中, 各种结构类型得到较大发展。(3)唐松草属在毛茛科中有较特殊的地位。在

国均产,生于海拔 3000m 以上的高山地带。主产青藏高原、新疆、云南北部、四川西部、陕甘宁等高山草地。其中 *T. alpinum* var. *alpinum* 向北达北极,向西达欧洲。亚属 2 全世界有 80 余种,亚洲仅一种,产我国西南地区。

由此可见,我国是世界唐松草属植物的一个分布中心。所产植物种与其它地区相比属于较原始的类群,且在越原始的组中特有种越多。西南为其主要分布区,各组间无明显地理隔离现象。

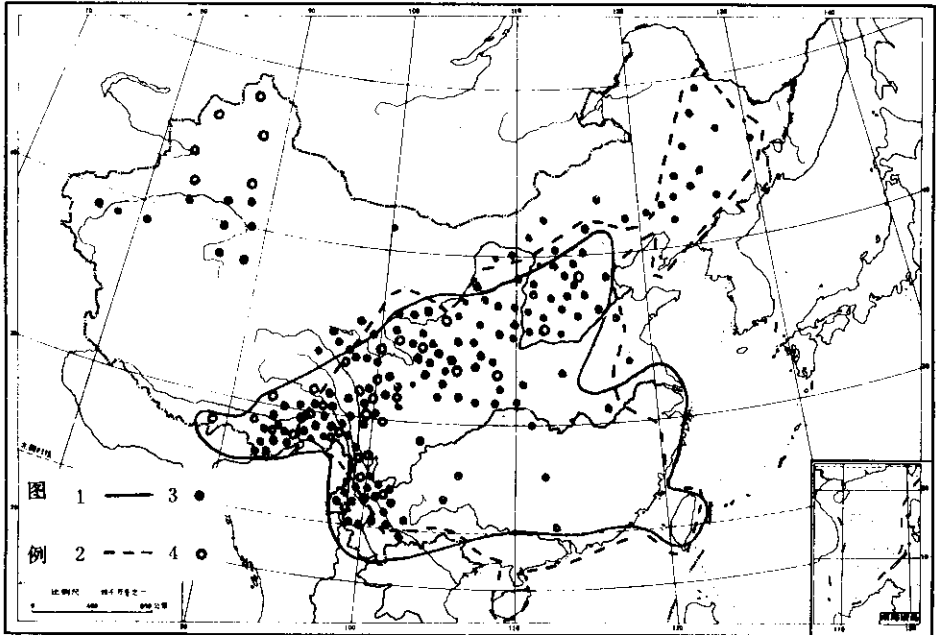


图 1 唐松草属植物在中国的分布

Fig.1 Distribution of *Thalictrum* Plants in China

1. Sect. *Leptostigma*; 2. Sect. *Tripterium*; 3. Sect. *Thalictrum*; 4. Sect. *Schlagintweitella*.

二、化学结构类型的分布及生理活性

大多数唐松草属植物主含生物碱,但也有少数种少含或不含。在生物碱中基本为苄基异喹啉衍生物,目前已发现 270 余个,分属异喹啉型、苄基异喹啉型、阿朴菲型、氧化阿朴菲型、原小檗碱型、普鲁托品型、巴威型、异巴威型、phenanthrenes 型、双苄基异喹啉型、阿朴菲-苄基异喹啉型、阿朴菲-巴威型等。其中各种双分子化合物大约有 120 余个,占化合物总数的 45% 左右。

中国唐松草属植物资源丰富,不少种作为民间草药。但化学工作做得还不够全面,一些特有种的成分还不清楚。为此,我们对国产 18 种唐松草的生物碱进行了含量测定(朱敏等,1989),并结合文献资料,对本属国产类群的成分及结构类型分布情况归纳于表 1 和

表 1 唐松草属的植物成分、民间疗效一览表

Table 1 Plants, Constituents and Folk Curative Effects of *Thalictrum*

植物学名 Latin name	化学成分 chemical constituents	参考文献 references
Subgen. 1 <i>Thalictrum</i> Sect. 1 <i>Leptostigma</i> <i>T. javanicum</i>	I [*] : magnoflorine III: jatrorrhizine demethyleneberberine palmatine columbamine thalifendine berberine IV: oxyberberine V: thalrugosaminine thalisopine IX: rugosinone	朱敏等, 1989 Bahadur et al., 1983; Sahei et al., 1985;
<i>T. ramosum</i>	berberine and other alkaloids	江苏植物所等, 1988; 肖培根等, 1965
<i>T. fortunei</i>	there is alkaloid reaction	江苏植物所等 1988; 肖培根等 1965
<i>T. omeiense</i>	IV: oxyberberine VI: methoxyadiantifoline thalmineline thaliadine thalmelatidine adiantifoline	辛文芬等 1983
<i>T. uncinulatum</i>	I: magnoflorine III: berberine jatrorrhizine	朱敏等 1989
<i>T. faberi</i>	I: magnoflorine III: berberine jatrorrhizine V: thalidasine N-desmethylthalidasine thaligosine O-methylthalibrine thaliracebine, thalifinine, O-methylthalicberine, thalrugosidine VI: thalifaberine, dehydrohuangshanine thalifalandine dehydrothalifaberine, faberonine, thalifaboremine, faberidine, thalifabine, huangshanine, thalifarapine, thalifabatine, thalifasine. IX: β -sitosterol	朱敏等 1989; 林隆泽等 1981; 1980; 王峰涛 1988; Lin et al., 1983; Wagner et al., 1984;
<i>T. rostellatum</i>	alkaloids can't be detected	朱敏等 1989
<i>T. atriplex</i>	I: magnoflorine III: coptisine, berberine, jatrorrhizine V: hernandezine, isotetrandrine VIII: cryptopine	朱敏等 1989
Sect. 2 <i>Tripterium</i> <i>T. reticulatum</i>	I: magnoflorine V: thalidezine isotetrandrine, hernandezine	朱敏等 1989
<i>T. baicalense</i>	I: baicalidine, glaucine, thabaicalidine, magnoflorine, baicaline II: 7-oxobaicalidine III: berberine	朱敏等 1989; 陆燕 著 1984; Mackh et al. 1982; 1983;
<i>T. petaloideum</i>	I: magnoflorine, III: jatrorrhizine, berberine palmatine VII: cryptopine	朱敏等 1989 Tomimatsu 1976;

续表 1

植物学名 Latin name	化学成分 chemical constituents	参考文献 references
<i>T. aquilegifolium</i> var. <i>sibiricum</i>	I: magnoflorine isocorydine, V: β -methylthalicberine, IX: quercetin, kaempferol, thamidine cyanogenic glycoside, caffeic acid, thalictoside, thalmine p-coumaric acid sinapic acid, ferulic acid, aquilegifolin.	吉林中药所 1982; 饭田英夫 1977; 朱敏等 1989; Sharples 1972; Tomimatsu 1976;
<i>T. przewalskii</i>	there is a alkaloid reaction	肖培根等 1965;
<i>T. urbainii</i>	I: S-(+)-oconovine, S-(+)-isocorydine.	Chen 1977;
<i>T. acutifolium</i>	I: acutifolidine, trilobinine, IV: oxoberberine, IX: methylpalmitate, cis-9-cis-12-methyloctadecadienoate nonacosane, n-pentatriacontane, β -sitosterol	林翠梧等 1989
<i>T. ichangense</i>	I: dehydroglaucine, glaucine, thalicsimidine, thaliciporphine, dehydrothalicsimidine	吴知行等 1988
<i>T. tuberiferum</i>	III: berberine,	Hyung 1965;
<i>T. filamentosum</i>	I: glaucine, thalicsimidine, V: thalisimine, dehydrothalisimine	Umarov et al, 1976;
<i>T. microgynum</i>	III: jatrorrhizine, V: berbamine, VII: allocryptopine, protopine, cryptopine	朱敏等 1989
Sect.3 Thalicttrum <i>T. leuconotum</i>	I: magnoflorine	朱敏等 1989
<i>T. vivgatum</i>	there is alkaloid reaction	肖培根等 1965
<i>T. viscosum</i>	III: berberine	江苏植物所 1988
<i>T. glandulosissimum</i>	I: magnoflorine III: berberine, coptisine, IV: oxocoptosine V: thalidezine, isothalidezine, hernandezine, izmirine o-methylthalidrine VII: protopine, cryptopine	朱敏等 1989 饶畅等 1989
<i>T. delavayi</i>	I: magnoflorine, glaucine III: jatrorrhizine, berberine V: thalidezine, isothalidezine, hernandezine,	朱敏等 1989
<i>T. reniforme</i>	there is alkaloid reaction	肖培根等 1965
<i>T. trichopus</i>	there is alkaloid reaction	肖培根等 1965

续表 I

植物学名 Latin name	化学成分 chemical constituents	参考文献 references
<i>T. foliolosum</i>	I: N, O, O-trimethylsparsiflorine, magnoflorine, xanthoplanine III: jatrorrhizine, thalifendine, columbamine, thalidastine dehydrodiscretamine berberine, plamatine IV: oxyberberine V: thalrugosidine thalrugosamine, thalidasine thaliosopine, thalirugidine, VI: thalicarpine IX: tembetarine, reticuline, rugosinone noroxyhydrastinine	朱敏等 1989 Bhakuni et al, 1982; Chattopadhyay et al, 1983; 1981; Tomimatsu 1976;
<i>T. finetii</i>	I: magnoflorine III: berberine, jatrorrhizine V: hernandezine, isotetrandrine, VII: protopine,	朱敏等 1989
<i>T. cultratum</i>	I: magnoflorine III: berberine V: (-)-5-hydroxythalidasine-2- α -N-oxide thalpindione, (+)-neothaliberine-2'- α -N-oxide, (-)-thalmiculine, (-)-thaligosine-2- α -N-oxide, (-)-5-hydroxythalidasine, (+)-thalidasine-2- α -N-oxide, (+)-2'-nortaliphylline, (-)-thalrugosaminine-2- α -N-oxide thalrugosinone, (+)-thaliphylline-2'- β -N-oxide(+)-2'-norox-yacanthine, (-)-5-hydroxythallmine, (+)-thamiculine thalrugosine, (-)-thalmiculimine, (+)-thalmiculatimine, (+)-cultithalminine VI: (+)-thalifaramine (+)-thalifaretine (+)-thalifarcine (+)-thalifaroline (+)-thalifarazine (+)-thalibulamine, (+)-thalifarone	Hussain et al, 1986; 1985; Wagner et al, 1987;
<i>T. cirrhosum</i>	III: berberine	江苏植物所等, 1988
<i>T. foetidum</i>	I: isoboldine, thalimidine, magnoflorine, glaucine II: oxoglucine, III: berberine. V: fetidine, thalfoetidine, isotetrandrine berbamine thalphine, thalpinine VI: phetidine others: harmine, better substance tannin substances volatile oil saponins, heart glucoside, ascorbic acid, orgri orgnic acid, flavoniods, cyclofoetigenin A	Abdizhabbarove et al. 1968; 1970; Ganenko et al. 1985; Ismailov et al. 1966; Mollov et al. 1966; 1967; Mukhamedova et al. 1981; 1983; Nuralieva et al. 1967; 1970; Sargazakov et al. 1963; Zatorskaya et al. 1972;

续表 1

植物学名 Latin name	化学成分 chemical constituents	参考文献 references
<i>T. isopyroides</i>	<p>I: dehydrothalicmine, cabudine, thalisopinine, thalioporphine preocoteine, N-methylauro- tetanine, delporphine, isoboldine, magnoflorine, N-methylcassythine, ocoteine,</p> <p>II: thalicminine,</p> <p>III: berberine</p> <p>V: thaligosinine, thalisopidine, thalisopine</p> <p>VII: cryptopine</p> <p>others: talmidine, 1-oxo-2-methyl-6, 7-demethoxy-1, 2-dihydro-isoquinonine</p>	<p>Abdizhabbarove et al. 1978; Ismailov et al. 1959; 1961; 1963; Kurbanova et al. 1975; Maekh et al. 1971; Pulatove et al. 1968;</p>
<i>T. minus</i>	<p>III: plamatine, jatrorrhizine, berberine, L-canadine, N-methylcanadine hydroxide</p> <p>I: glaucine, N-oxide-thalicminine, N-oxide-thalicmidine, magnoflorine, corydine, thaliadine, N-oxidepreocoteine, thalicmine, thalicmidine ocoteine, thalicsimidine</p> <p>II: thalicminine,</p> <p>V: thalidazine, thalphenine, O-methylthalmethine, O-methylthalicbenine, O-methylthalicberine, aro-moline thalmethine, thalicberine</p> <p>VI: thalmelatine, thalcarpine, thalmineline thalipine (+)-istanbulamine (+)-iznikine,</p> <p>VII: allocryptopine</p> <p>VIII: argemonine, N-methylargemonine, eschscholizidine</p>	<p>朱敏等, 1989 Dutschewska et al. 1982; 1966; Duchevska et al. 1980; 1971; Johannes et al. 1970; Shamm, et al. 1969; Kaniewska et al. 1971; Kuchkova et al. 1965; Mollov et al. 1966; 1971 Mukhamedova et al. 1983; Muraveva et al. 1985; Pulatove et al. 1966; 1967; Sidzhimov et al. 1986; Shakhabutdinova et al. 1967; Sidjimov et al. 1984; Umarov et al. 1977;</p>
<i>T. simplex</i>	<p>I: thalsimidine, ocoteine, magnoflorine, thalicsimidine,</p> <p>II: thalicminine</p> <p>III: thalmethine, hernandezine, thalidezine, thalcimine, O-methylthalmethine, thalsimine</p> <p>VII: allocryptopine</p> <p>IX: thalicticine</p>	<p>朱敏等 1989 肖培根等 1965 Tomimatsu 1976; Wu et al. 1980;</p>
<i>T. flavum</i>	<p>I: magnoflorine thalicsine</p> <p>III: berberine canadine jatrorrhizine</p> <p>V: hernandezine</p> <p>VI: thalcarpine</p> <p>VII: cryptopine</p> <p>IX: thalflavine, thalflavidine</p>	<p>江苏植物所等 1988 Tomimatsu 1976; Dutschewska et al., 1982;</p>
<i>T. squarrosus</i>	<p>I: magnoflorine</p> <p>III: berberine,</p> <p>V: thalidasine</p>	<p>王峥涛 1988, 吉林中药所 1982 Sobiczewska et al. 1970;</p>

续表 1

植物学名 Latin name	化学成分 chemical constituents	参考文献 references
Sect.4 Schtagintweitella <i>T. squamiferum</i>	some alkaloids in roots	肖培根等 1965
<i>T. alpinum</i>	I: O-methylisoboldine isoboldine magnoflorine III: berberine columbamine jatrorrhizine palmatine thalifendine IV: oxyberberine V: thapindione, N-desmethylthalarugosidine thalidasine thalarugosidine, thalarugosaminine, neothalibrine hernandezine VI: thalicarpine	Ismailov et al. 1966; Tomimatsu 1976; Wu et al. 1980;
Subgen.2 <i>Lecoyerium</i> <i>T. simithii</i>	I: magnoflorine III: berberine jatrorrhizine VII: cryptopine V: hernandezine	朱敏等 1989

* I = aporphine, II = oxoaporphine, III = protoberberine, IV = oxyberberine, V = bisbenzylisoquinoline, VI = aporphine-benzylisoquinoline, VII = protopine, VIII = pavine, IX = other alkaloids.

表 2 化合物类型在植物中的分布

Table 2 Distribution of chemical structure types in sections

植物分类单位 taxon	种 数 number of species	药用种数 number of medicinal species	化合物类型 chemical structure types								
			I *	II	III	IV	V	VI	VII	VIII	IX
1. Sect. Leptostigma	18	6	1	—	7	1	13	17	1	—	1
2. Sect. Tripterium	19	9	15	1	3	1	8	0	3	—	4
3. Sect. Thalictrum	27	15	27	2	10	2	37	18	6	2	6
4. Sect. Schlagintweitella	2	2	3	—	5	1	7	1	—	—	2
Subgen. <i>Lecoyerium</i>	1	1	1	—	2	—	1	—	1	—	—

* 代号见表 1 see Tab.1 for the code I = 阿朴菲型, II = 氧化阿朴菲型, III = 原小檗碱型, IV = 氧化小檗碱型, V = 双苄基异喹啉型, VI = 阿朴菲-苄基异喹啉型; VII = 普鲁托品型; VIII = 巴威型, IX = 其它类生物碱.

表 2, 得到以下结论:

1. 唐松草属是双苄基异喹啉(简称 BBI)生物碱等双分子化合物的重要分布中心。在 BBI 结构中, 两个 BI 分子有单、双、三醚键相连的三种方式。但在唐松草属中仅存在单、双醚键相连的两种。在国产种中除金丝马尾连 *T. glandulosissimum* 中发现有 2 个单醚键相连的化合物外(饶畅等, 1989), 其它均为双醚键相连。

本属所含阿朴菲衍生物数目不少, 而氧化阿朴菲型则不多, 国产种中只发现了三个。原小檗碱型衍生物大部分为季铵碱, 并有部分 8 位为羰基的氧化小檗碱型存在, 仅有少数种存在着四氢小檗碱型衍生物。

2. 在第一亚属的四个组中, 各结构类型在不同组中所占比例不同。组 1 中双分子化合物占比很大, 其中阿朴菲-苄基异喹啉(简称 ABI)型又比 BBI 型更多。如在峨眉唐

松草 *T. omeiense* 中所得双分子化合物均为 ABI 型,而在大叶唐松草 *T. faberi* 中分离的 20 个双分子化合物里 12 个为 ABI 型,8 个为 BBI 型。

与形态上的差异相似,组 2 在化学上与其它组相比也有一定特殊性。所含生物碱的类型以阿朴菲为主,同时也有一些 BBI 型存在,但目前尚未发现 ABI 的存在。其特殊性表现在本组植物含有大量非生物碱化合物。如唐松草 *T. aquilegifolium* var. *sibiricum* 中只分离出两个阿朴菲碱,其它均为有机酸、黄酮、甙等化合物。在尖叶唐松草 *T. acutifolium* 分离的八个化合物中只有三个生物碱,其它多为长链碳氢化合物。这组植物由于含生物碱较少,作为药用的种也不多。

组 3 是生物碱较集中分布的类群,但在组内较原始的系中,生物碱的含量并不高。如系 1 的白茎唐松草 *T. leuconotum* 生物碱含量低于 0.001%。而在较进化的系中,生物碱的含量较高。出现一些总碱达 2% 以上的高含量种。本组化合物的结构类型和数目比前两组均有较大增加,尤以双分子化合物为多,其中 BBI 比 ABI 多一倍以上。

组 4 所含生物碱与组 3 相似,以 BBI 的数目为多。亚属 2 我国产一种,含量测定结果与组 3 相仿。

3. 生物碱的含量与植物进化有一定关系。越进化的组,特化的结构类型越多,从而也导致了多样的药理作用。如 BBI 和 ABI 生物碱多具有降压、抗菌、抗癌、抗心律失常、解痉、松弛肌肉等作用;阿朴菲型有镇痛、镇静、抗菌、降压等活性;原小檗碱型具有抗菌作用。药理实验还证明不少植物的总提物有抗癌、抗菌等活性。因而本属是开发这类活性成分的重要资源。

三、讨 论

1. 毛茛科中,苄基异喹啉生物碱集中于唐松草亚科内,特别是唐松草属和黄连属,尤以唐松草属存在的结构类型最多。它在化学上除有其它含苄基异喹啉的属中普遍存在的阿朴菲和原小檗碱型外,以富含双苄基异喹啉为其特征。同时还存在着普鲁托品型、巴威型等。这些成分在本科其它属中极少发现。在形态上,本属为瘦果,而其它含这类碱的属多表现为蓇葖果。科内除本属外的瘦果群中则极少发现苄基异喹啉碱。此外在台湾产的 *T. sessile* 种中还发现了在翠雀族中普遍存在的二萜类生物碱(Wu Yang-chang, 1988)。这些现象说明唐松草属在毛茛科中占有较特殊的地位,它是联系蓇葖果和瘦果植物群的过渡类型。它在成分上更近于蓇葖果群,而在形态上又与瘦果群有密切联系。

在唐松草亚科内,唐松草族与耧斗菜族、黄连族在成分上联系密切。耧斗菜族以黄酮为主要成分,但已产生少量的阿朴菲、原小檗碱和双苄基异喹啉型衍生物,其总碱含量低于 0.1%,在唐松草族中,生物碱在大多数种中已成为主要成分。上列三类生物碱从数目和含量上都得到很大发展,同时还产生出 ABI 及普鲁托品型等多种结构。总碱最高可达 2% 左右。当发展到黄连族时,生物碱在所有种中均为主要成分。化合物类型集中表现为原小檗碱型,总碱最高可达 12%。这表现化学成分的确随形态的不断进化而在质和量上不断变化着。

2. 毛茛科在 Dahlgren (1980) 的分类系统中与小檗科、防己科、罂粟科同归于毛茛超目中。它们在化学成分上有着密切的联系。而这些联系都能在唐松草属中得到最好体

现。如与小檗科相似,本属存在着丰富的原小檗碱型和双苄基异喹啉型衍生物;与防己科类同,双苄基异喹啉型在属中占有显著的地位;本属许多种都含有普鲁托品型、巴威型、异巴威型衍生物,这些都反映了与罂粟科有一定亲缘关系。而在毛茛科的其它属中都不具有这种多样的相似性。从化学系统学观点看,正是基于成分上的共性,才使上述四科有机地结合起来。

3. 根据 Dutschewska et al. (1982) 的报道,国外将我国唐松草亚属的植物都放在 Sect. *Microgynes* Lec. 中的同一亚组 Subsect. *Longistamine* Lec. 中。而中国植物志则根据我国情况分为四个组。从我们的化学分析结果看,上述四组的划分及亲缘关系的安排是合理的。无论从形态上还是从成分上都体现出组 1 是基础,组 2 为一单独分枝,组 3 是联系组 1 与组 4 及亚属 2 的重要环节这一特点。

总之,本属所含的化学成分在科内及科间的系统安排上均起重要作用。属内各组所含成分有一定规律可循。因此深入开展我国特有种的研究,将对全面了解世界唐松草属概况和充分利用这一资源十分有益。

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